Low Phosphorus Concentrations in Si by Diffusion from Doped Oxide Layers

J. Middelhoek and J. Holleman

Twente University of Technology, Enschede, The Netherlands

ABSTRACT

The diffusion of phosphorus into silicon from doped oxide layers, deposited at low temperatures, has been studied in order to achieve reproducible impurity distributions with surface concentrations varying from 5×10^{15} to 10^{18} atoms/cm^3. Special attention has been given to the differences arising from indiffusion in an N_2 or in an O_2 ambient. The dependence on the temperature of the diffusion coefficients of phosphorus in silicon and in silicon dioxide is determined at a surface concentration of 5×10^{16} atoms/cm^3.

Doped and undoped oxide layers, which are formed by the oxidation with O_2 of the hydrides of Si, P, B, and other elements at the surface of a slice of monocrystalline silicon at a characteristic temperature of 400°C have valuable applications in the manufacture of integrated circuits (1-4).

The application as a diffusion source is particularly interesting, because an independent control of the surface concentration over several orders of magnitude is made possible.

The purpose of this research is to find the practical lower limit of the phosphorus concentration, which can be obtained by indiffusion. Our research forms an extension of the work of Barry *et al.* (5-7). He reported surface concentrations of phosphorus varying from 6×10^{17} to 2×10^{20} atoms/cm^3. Moreover we also studied the differences which arise when the indiffusion takes place either in an N_2 or in an O_2 ambient. In particular the indiffusion in an O_2 atmosphere has important applications in integrated circuit technology.

Usually a thin layer of undoped oxide is already present on the surface of the substrate before deposition of the oxide. This is caused by air oxidation or due to a cleaning step in nitric acid. The influence of this barrier layer on the result of the diffusion has been carefully observed.

The temperature dependence of the diffusion coefficients of P on Si and SiO_2 has been studied in view of process control. Activation energy values of importance from a theoretical point of view might be expected due to the method of diffusion and on account of the low concentrations.

Theory

Barry and Olofsen (5) have given a detailed mathematical description of a model for the evaluation of the diffusion from a doped oxide layer. We shall use the same model and notation. Figure 1 shows a schematic representation of the different layers together with the diffusion parameters.

The expected impurity distribution after indiffusion from an infinitely thick source layer and without a barrier layer present, is

$$C_2(x,t) = C_o[m\sqrt{D_1}/(m\sqrt{D_2} + \sqrt{D_1})] \operatorname{erfc} x/2\sqrt{D_2 t} \quad [1]$$

The segregation constant m is defined by the equation $m = C_2(0,t)/C_1(0,t)$. Throughout this paper we will use the approximation

$$m\sqrt{D_1}/(m\sqrt{D_2} + \sqrt{D_1}) = \sqrt{D_1}/\sqrt{D_2} \quad [2]$$

because in the case of phosphorus, the data from literature (7, 9) indicate that $\sqrt{D_2} >> \sqrt{D_1}$ and $m >> 1$.

When a first correction term for a finite thickness of the source layer x_o is added we arrive at

$$C_2(x,t) = C_o\sqrt{D_1}/\sqrt{D_2}[\operatorname{erfc} x/2\sqrt{D_2 t} - 2 \operatorname{erfc} (x/2\sqrt{D_2 t} + x_o/2\sqrt{D_1 t})] \quad [3]$$

The decrease of the total amount of indiffused atoms due to a finite thickness is less than 1% if $x_o > 4\sqrt{D_1 t}$. It is useful to express x_o in this inequality as a fraction of the desired junction depth x_j. Using the approximation $x_j \simeq 4\sqrt{D_2 t}$, we find as a general rule

$$x_o > x_j\sqrt{D_1/D_2} \quad [4]$$

Using Barry's results (7), we find that in the case of phosphorus no decrease is apparent when

$$x_o > 0.05 x_j. \quad [5]$$

When a thin, undoped oxide layer is present between the silicon slice and the doped source layer, caused, for instance, by a cleaning procedure, the distribution in the silicon may still be described as a complementary error-function.

$$C_2(x,t) = C_o\sqrt{D_1/D_2} \operatorname{erfc} (x + x_B\sqrt{D_2/D_1})/(2\sqrt{D_2 t}) \quad [6]$$

Contrary to expression [1] the surface concentration is now time-dependent

$$C_2(0,t) = C_o\sqrt{D_1/D_2} \operatorname{erfc} x_B/2\sqrt{D_1 t} \quad [7]$$

The distribution in the silicon is equal to the profile arrived at when, from a pure complementary error-function profile, a top layer with a thickness of $x_B\sqrt{D_2/D_1}$ has been removed by a sectioning technique. Irvin (8) has composed a set of graphs which can be used for the evaluation of profiles obtained by sectioning. These graphs are also applicable in the case of the presence of an undoped barrier layer, provided that $x_B\sqrt{D_2/D_1}$ is known.

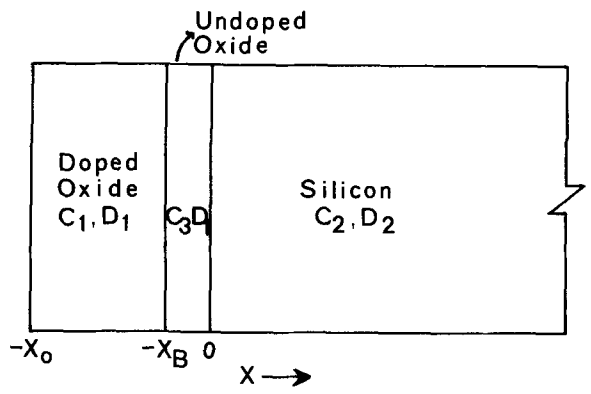

Fig. 1. Diffusion from a deposited doped oxide through a barrier oxide into a semiconductor substrate.

Key words: impurity distribution, low surface concentration, chemical vapor deposition, MOS channels, IC fabrication.

The above solutions are applicable for diffusion in the presence of constant barrier thickness. However, in an oxidizing ambient, an undoped oxide layer grows between the deposited layer of doped oxide and the silicon slice. What occurs can be physically clarified without a thorough mathematical explanation.

The rate of the barrier growth can be derived from the well-known parabolic law for thermal oxidation (9) when the thickness x_o of the deposited layer is also taken into account

$$(x_o + x_B)^2 = B(t_i + t), \text{ where } (x_o + x_{Bo})^2 = Bt_i$$

The parabolic rate constant B is proportional to the diffusion constant of the oxidizing species. By approximation

$$x_B = x_{Bo} + Bt/2x_o \quad [8]$$

The progress of the diffusion in the SiO_2 barrier is difficult to characterize precisely. We take $2\sqrt{D_1 t}$ as the distance covered, which is a reasonable assumption as $x_B > \sqrt{D_1 t}$. In Fig. 2 we plotted x_B and $2\sqrt{D_1 t}$ in one graph as function of the time. What occurs can be clearly seen. Initially the diffusion progresses more quickly than the barrier increases, but after some time the barrier growth overtakes the diffusion of the dopant. At the moment that the processes have the same velocity, the indiffusion into the silicon ceases. The total amount of indiffused impurity remains constant and by further high temperature treatment the distribution begins to approach a Gaussian profile.

Experimental Details

Standard Monsanto silicon slices, doped with boron to a specific resistivity of about 10 ohm-cm plane direction (100), with one side polished and the other side lapped, were used in this research. The specific resistivity of each slice was determined before the experiments and the dopant concentration was derived from literature data (9).

The pretreatment of the slices comprised treatments in fuming nitric acid and in boiling nitric acid (65%), rinsing and centrifuging until dry. Directly afterwards, the deposition in the reactor was carried out.

The depositions were performed in a home-made, one-slice reactor at a slice temperature of 325° ± 2°C. The reactor was cylindrical with a height of 20 cm and a diameter of 8 cm. Before the deposition the reactor was purged with N_2 and the slice preheated for 2 min. The gas flows were argon: 7 liter/min; O_2: 35 ml/min; SiH_4 (net): 7 ml/min. The gas flow of PH_3 varied. The dilution in the cylinder used was 6 ppm. The dilution of SiH_4 in A was 1%.

At first a uniform phosphorus-doped oxide layer of 4000Å was deposited at a rate of 1000 Å/min. Thereafter a densification step (10) followed during 10 min at 650°C in N_2, wetted by leading the gas flow through a washing-bottle containing water at room temperature. This step has been proved to be essential for achieving good diode characteristics in the fabrication of MOS transistors.

Finally, the phosphorus-doped layer was covered by another deposited layer of 4000Å. This layer configuration is also applied in the fabrication of MOS transistors.

After diffusion the oxide was etched away and the sheet resistance was determined with a four point probe. The junction was made visible (12) by grinding a circular groove with a steel ball and by staining one of the layers with $AgNO_3$ or Fuller and Ditzenberger's etching fluid (12). The junction depth was determined with the measuring ocular of a light-microscope.

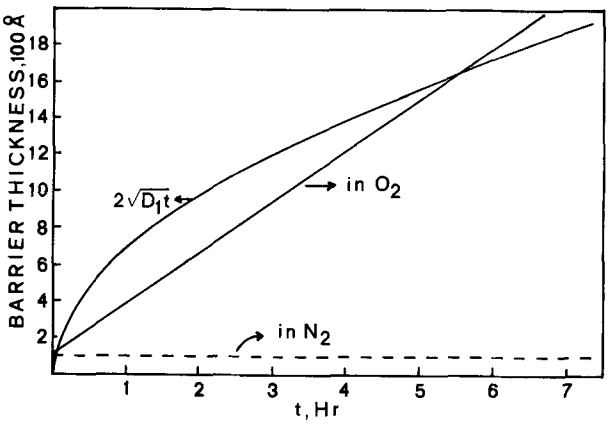

Fig. 2. The increase of the barrier thickness and of the diffusion length of phosphorus in oxide vs. time.

Evaluation Method

The theoretical conditions for an evaluation of the indiffusion based on the combined measurement of junction depths and sheet conductivities, assuming an erfc distribution, are excellent. The background as well as the diffusant concentrations are in this research always much smaller than the intrinsic carrier concentrations at the diffusion temperatures. Complications (14-16) due to an internal field and variation of the vacancy concentration do not occur.

For the justification of the diffusion model it is not only necessary to investigate the variation of x_j and R_s^{-1} with diffusion time, but also the variation with the concentration of dopant in the oxide. It is essential that the surface concentration is proportional to the initial dopant concentration in the source layer (1).

The expression for the junction depth, as derived from [6], is

$$x_j = -x_B\sqrt{D_2/D_1} + 2\sqrt{D_2 t}\ \text{argerfc}\ C_B\sqrt{D_2}/C_o\sqrt{D_1} \quad [9]$$

The value, x_B, of the thickness of the thin oxide barrier in this research is not determined separately. It has an estimated value (2, 5) between 15 and 50Å. The expected intercept with the ordinate of the curve x_j *vs.* $\sqrt{t}$ is, according to the diffusivity values reported by Barry (7), very small, about 1000Å. The determination of this intercept cannot be done accurately because systematic errors in the junction depth measurement are of the same order of magnitude. However the determination of $x_B\sqrt{D_2/D_1}$ is made possible by comparing the systematic difference of two series of measurements of x_j *vs.* C_o. The wafers of one series were dipped in a SiO_2 etchant just before the deposition of the doped oxide layer. The wafers of the other series are covered with the thin oxide layer normally found after a cleaning step with HNO_3.

The total amount (6, 9) of indiffused atoms Q is in the case of a complementary error function distribution

$$Q(t,C_o) = 2\pi^{-1/2}C_s\sqrt{D_2 t} = 2\pi^{-1/2}C_o\sqrt{D_1 t} \quad [10]$$

For very low concentrations compared with the background concentration, three corrections have to be made. First the integral may not be extended to infinity. For finite thickness of x_j the expression for Q can be completed with a factor (11) (Fig. 3)

$$F = (1 - \sqrt{\pi}\ \text{ierfc}\ x_j/2\sqrt{D_2 t}) \quad [11]$$

Secondly an amount x_jC_B must be subtracted for the compensation of the background concentration. Thirdly when an undoped barrier layer is present, an amount x_BC_o must also be subtracted because this thin undoped barrier layer acts to a first approximation as a source for a Gaussian distribution, but then in a negative sense.

Thus, the amount of indiffused atoms, which can be determined by sheet conductivity measurements is

$$Q = 2\pi^{-1/2}C_oF\sqrt{D_1 t} - x_jC_B - x_BC_o \quad [12]$$

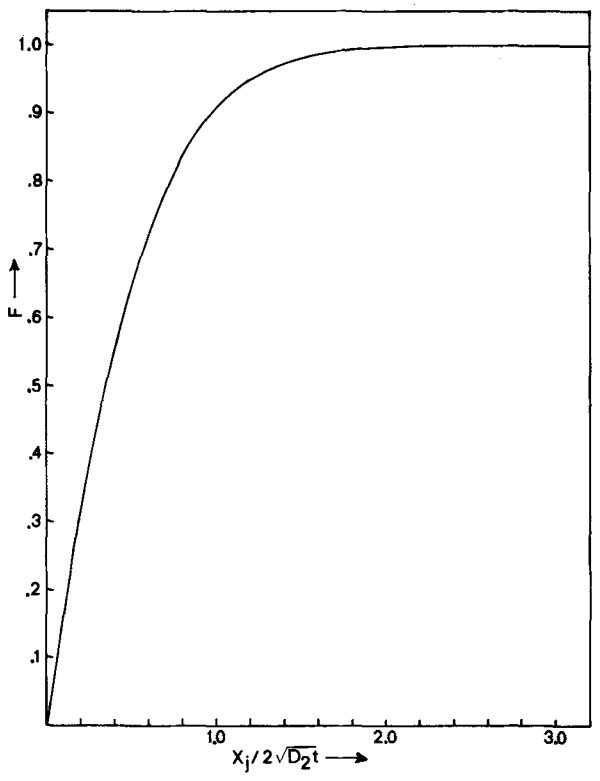

Fig. 3. The factor *F*, which accounts for the indiffused atoms beyond the metallurgical junction, *vs.* $x_j/2\sqrt{D_2t}$.

The sheet conductivity R_s^{-1} would be a linear function of Q, if the mobility of the charge carriers, in this case electrons, was independent of the concentration. This problem is usually circumvented by using Irvin's graphs (8) for the evaluation in which this mobility variation is taken into account. But it is however, interesting to check how this mobility variation influences the evaluation. The sheet conductivity as well as the surface concentration determined with Irvin's graphs will therefore be plotted *vs.* the dopant concentration in the oxide. Thereby we shall assume that in our reactor system the following relation is valid for small PH_3/SiH_4 ratios

$$C_o = (PH_3/SiH_4)K2 \cdot 3 \times 10^{22} \text{ atoms/cm}^3 \quad [13]$$

K is a reactor constant. Therefore we evaluate according to

$$R_s^{-1} = K^*\sqrt{D_1 t}\,(PH_3/SiH_4) \quad [14]$$

Results and Discussion

In Fig. 4 and 5 the experimentally found junction depth x_j and the sheet conductivity $(R_s)^{-1}$ are both represented as functions of the square root of the time. The graphs show straight lines for diffusion in N_2 as expected according to Eq. [9] and [14] for diffusions in an inert atmosphere.

The intercept of the curve x_j *vs.* $\sqrt{t}$ is smaller than 1000Å and can not be accurately determined from these experiments.

When the diffusion was performed in an oxygen ambient, the junction depths for longer times are somewhat smaller than the values found in N_2. This is obviously an indication that the amount of indiffused phosphorus atoms is smaller. This is even more evident from the sheet conductivity plot (Fig. 5). By diffusion after a certain time in O_2 the sheet conductivity remains constant. This is a result of the cut-off of further influx caused by the growth of an undoped barrier as explained in the theoretical section (Fig. 2).

The sheet conductivity after indiffusion in N_2 for longer times also remains below the value predicted by theory. This may be due partly to exhaustion of the source layer, because $x_o = 4000$Å and $x_j = 10\mu$ and, according to [5], exhaustion should lead to a small decrease of the sheet conductivity.

The average specific conductivity of the layers $(R_s x_j)^{-1}$ is equal to the quotient of the slopes of the

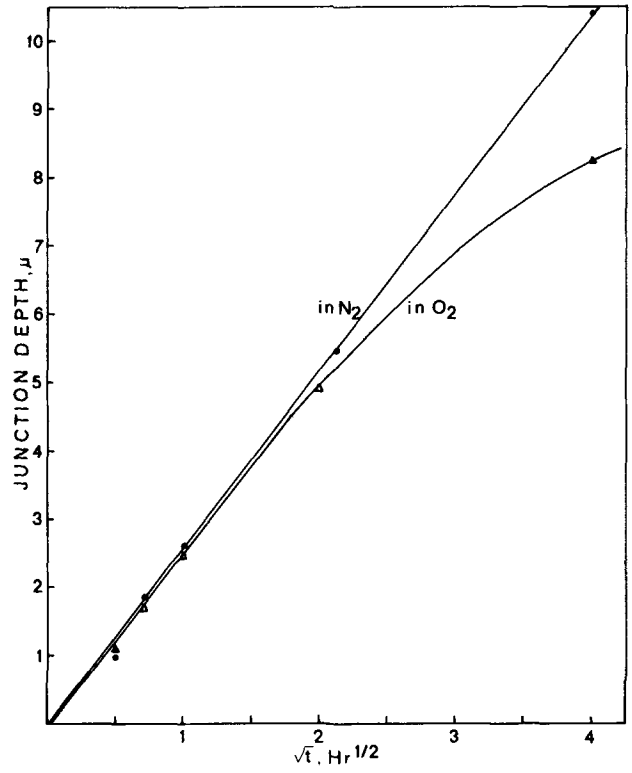

Fig. 4. Junction depths resulting from P diffusion into Si from deposited oxides at 1200°C in an N_2 or in an O_2 ambient, *vs.* time. $PH_3/SiH_4 = 2.34 \times 10^{-4}$. $C_s = 4.8 \times 10^{17}$ atoms/cm^3.

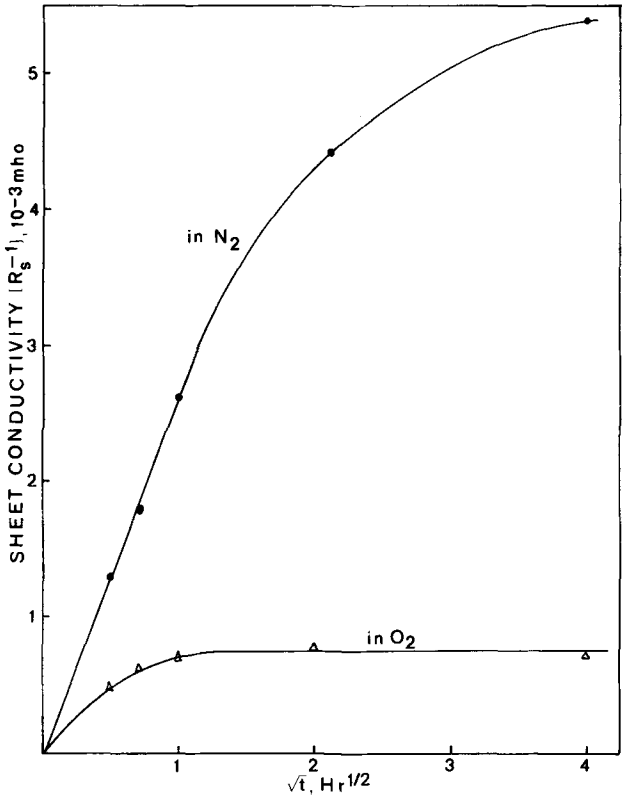

Fig. 5. Sheet conductivities resulting from P diffusion into Si from deposited oxides at 1200°C in an N_2 or in an O_2 ambient, *vs.* time. $PH_3/SiH_4 = 2.34 \times 10^{-4}$. C_s 4.8 x 10^{17} atoms/cm^3.

respective curves. It is a constant for the layers diffused in N_2 as would be expected for a complementary error-function profile. With the help of Irvin's graphs (8) the surface concentration for the diffusion experiments in N_2, represented in Fig. 4 and 5, is found to be 4.8×10^{17} atoms/cm^3. The diffusivity of phosphorus in silicon at 1200° ± 1°C was calculated from the slope of the plot x_j *vs.* t and the found surface concentration. $\sqrt{D_2} = 0.60\ \mu/\text{hr}^{1/2}$.

Figures 6 and 7 show the result of comparable experiments, but with a much smaller phosphorus concentration C_o in the oxide. A pronounced difference occurs, when the slice before deposition, is either dipped or not dipped in an SiO_2 etchant. This was not the case with the above discussed concentration of 4.8×10^{17} atoms/cm^3. Evaluation of the surface concentration gives 3.0×10^{16} atoms/cm^3 when dipping is included and 8.5×10^{15} atoms/cm^3 without dipping. The diffusivities were respectively 0.52 and 0.56 $\mu/\text{hr}^{1/2}$. The concentration of PH_3 in the deposition gas was 8 times smaller for the experiments of Fig. 6 and 7, than for the experiments of Fig. 4 and 5. The resulting surface concentration was however 16 times smaller with dipping and 57 times smaller without dipping. This means that for this low concentration more than half of the amount of phosphorus is lost during the operation in the reactor system.

Diffusion in an oxygen ambient leads to irreproducible results at this low concentration.

The results of the experiments concerning the temperature dependence of the diffusivities are represented in Fig. 8 and Table I. From the slope of the curve ln $D_2^{1/2}$ *vs.* T^{-1} an activation energy of 5.00 ± 0.10 eV was calculated at a surface concentration of 5×10^{16} atoms/cm^3. Compared with other values from the literature (7, 13) such as 2.45 eV(2×10^{20}/cm^3); 3.78 eV(5×20^{18}/cm^3); 2.4 eV(9.5×10^{20}/cm^3; and 3.4 eV(3×10^{18}/cm^3) the value now found is much larger. The calculation of the activation energy depends mainly on the values found for the junction depth. The assumption of a systematic error in the junction depth of 0.45μ is necessary to bring the value for the activation energy into agreement with the values reported thus far in the literature for phosphorus diffusion.

The graph of ln R_s^{-1} *vs.* T^{-1} makes it possible, according to [14], to calculate the activation energy of the diffusion coefficient of phosphorus in the oxide. We found 2.04 ± 0.20 eV. It was assumed that the effective average mobility at 5×10^{16} atoms/cm^3 did not change very much. Literature data indicate a variation of less than 10% and the results, represented in Fig. 10, give reason to believe that the variation is even less. Barry (7) found 4 eV, but this value is not very accurate, as he states in his article, because it is calculated with the help of the barrier thickness x_B.

Barry (7) also found by independent measurements of C_o and C_s that the ratio $C_o/C_s = \sqrt{D_2/D_1}$ is independent of the temperature, but dependent on the concentration of the diffusant. This result is incompatible with his diffusion model. We found, however, in Table I that C_s decreases at a constant C_o and an increasing temperature, because D_2 has a greater increase with a rise in temperature than D_1.

Figures 9, 10, and 11 show the results of diffusion experiments at a constant diffusion time and temperature with varying concentrations of PH_3 in the deposi-

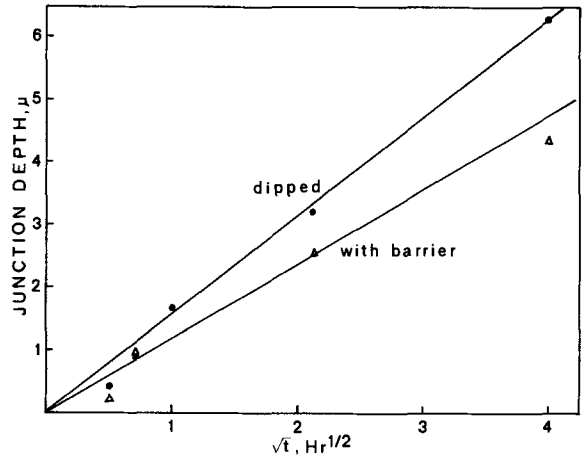

Fig. 6. Junction depths resulting from P diffusion into Si from deposited oxides at 1200°C in an N_2 ambient, *vs.* time. $PH_3/SiH_4 = 3 \times 10^{-5}$. After a cleaning step in HNO_3 the wafers of one series are dipped in an HF solution before the deposition of the doped oxide.

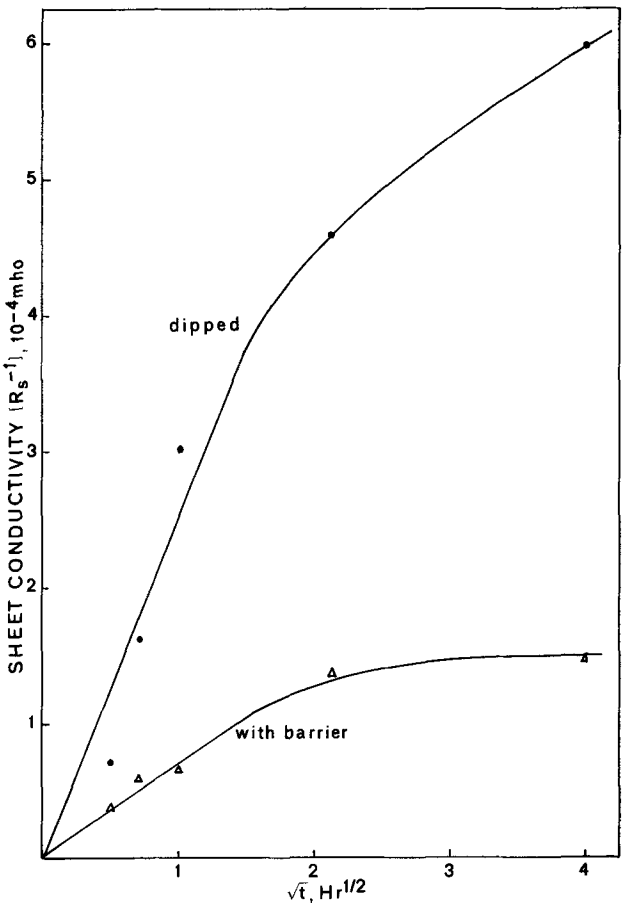

Fig. 7. Sheet conductivities resulting from P diffusion into Si from deposited oxide at 1200°C in an N_2 ambient, *vs.* time $PH_3/SiH_4 = 3 \times 10^{-5}$. After a cleaning step in HNO_3 the wafers of one series are dipped in an HF solution before the deposition of the doped oxide.

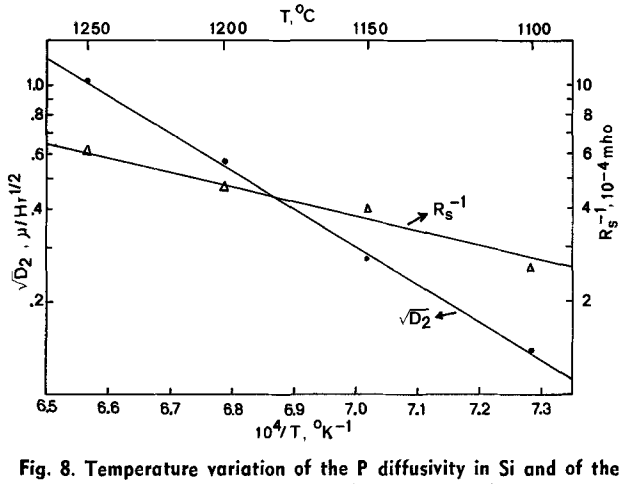

Fig. 8. Temperature variation of the P diffusivity in Si and of the sheet conductivity resulting from P diffusion into Si from deposited oxides during 125 min in an N_2 ambient. $PH_3/SiH_4 = 6.4 \times 10^{-5}$.

Table I. Temperature variation of the diffusion quantities resulting from P diffusion into Si from deposited oxides in an N_2 ambient. $PH_3/SiH_4 = 0.64 \times 10^{-4}$. Diffusion time is 125 min

Temp, °C	x_j, μ	R_s^{-1}, 10^{-4} mho	$(R_s x_j)^{-1}$, mho/cm	C_s, 10^{16} atoms/cm^3	$\sqrt{D_2}$, $\mu/hr^{1/2}$
1100	0.71	2.57	3.48	9.0	0.137
1152	1.35	4.00	2.96	6.8	0.272
1200	2.40	4.65	1.94	3.6	0.562
1250	4.34	6.18	1.42	2.5	1.037

tion gas. It was supposed that the concentration C_o was a linear function of the ratio PH_3/SiH_4 in the deposition gas (13). That this supposition was correct, is demonstrated in Fig. 10. According to the theory a linear relation is predicted between $(R_s)^{-1}$ and C_o, and a linear relation between $(R_s)^{-1}$ and (PH_3/SiH_4) is found.

At the highest concentrations a deviation occurs. This may be due to a smaller mobility at these concentrations. But this is not probable, because a similar deviation occurs by diffusion in an oxygen ambient, while the concentration is in a range, where no deviation occurs in the results obtained in an N_2 atmosphere. An error in the control of the PH_3 flow is more probable. The graph of the surface concentration *vs.* (PH_3/SiH_4) (Fig. 11) is not as straight as the graph $(R_s)^{-1}$ *vs.* (PH_3/SiH_4) (Fig. 10). It would appear that the dependence of the mobility on the concentration, such as taken into account by Irvin in his graphs (8) is exaggerated in the range of 10^{17}-10^{18} atoms/cm^3.

The systematic difference in junction depth between slices with etching and those without etching is obvious. This difference must correspond with $x_B\sqrt{D_2/D_1}$ (9). The series in N_2 show a difference of about 800Å

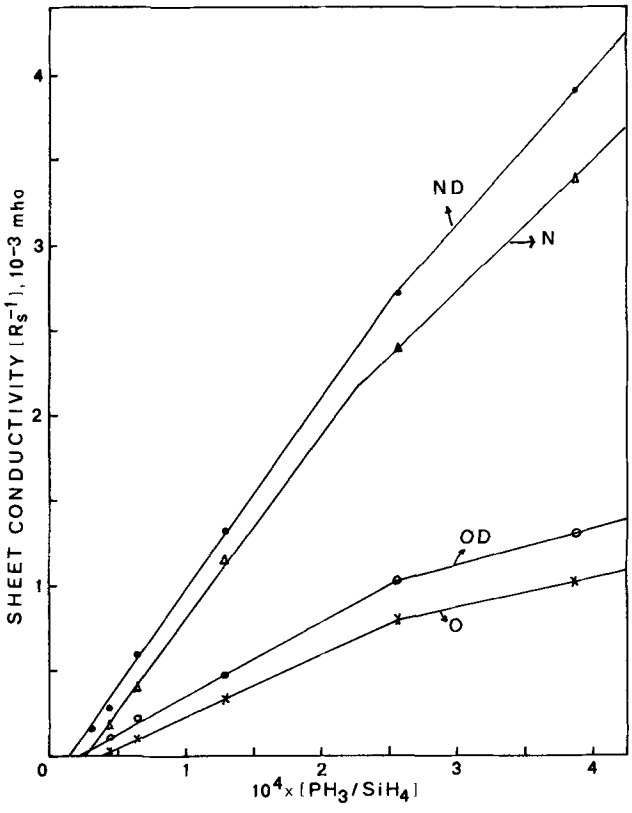

Fig. 10. Sheet conductivities, resulting from P diffusion into Si from deposited oxides during 43 min at 1200°C, *vs.* the PH_3/SiH_4 ratio in the deposition gas. For symbol definition see Fig. 9.

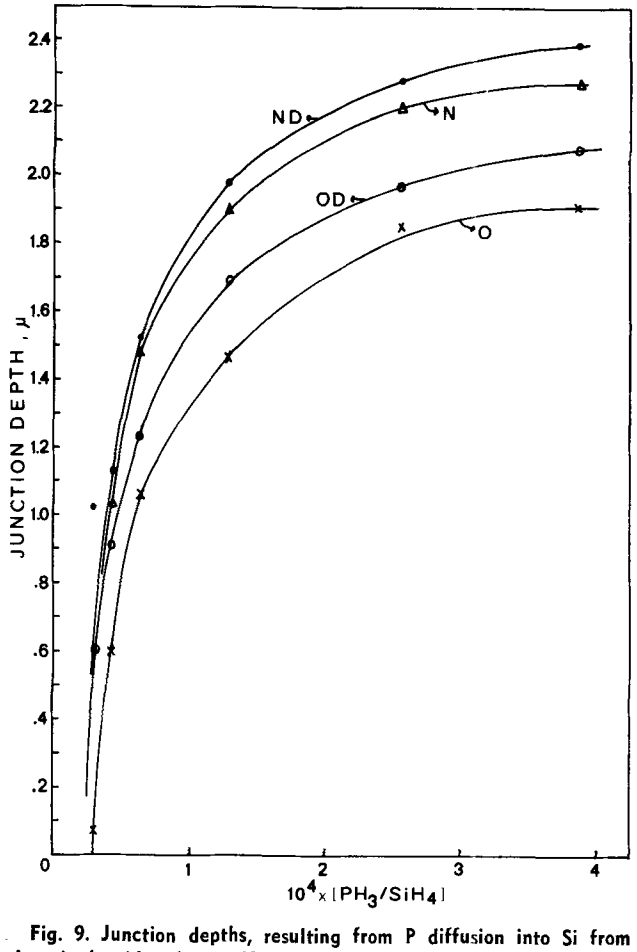

Fig. 9. Junction depths, resulting from P diffusion into Si from deposited oxides during 43 min at 1200°C, *vs.* the PH_3/SiH_4 ratio in the deposited gas. N: diffusion in an N_2 ambient. O: diffusion in an O_2 ambient. D: dipped in an HF solution before deposition.

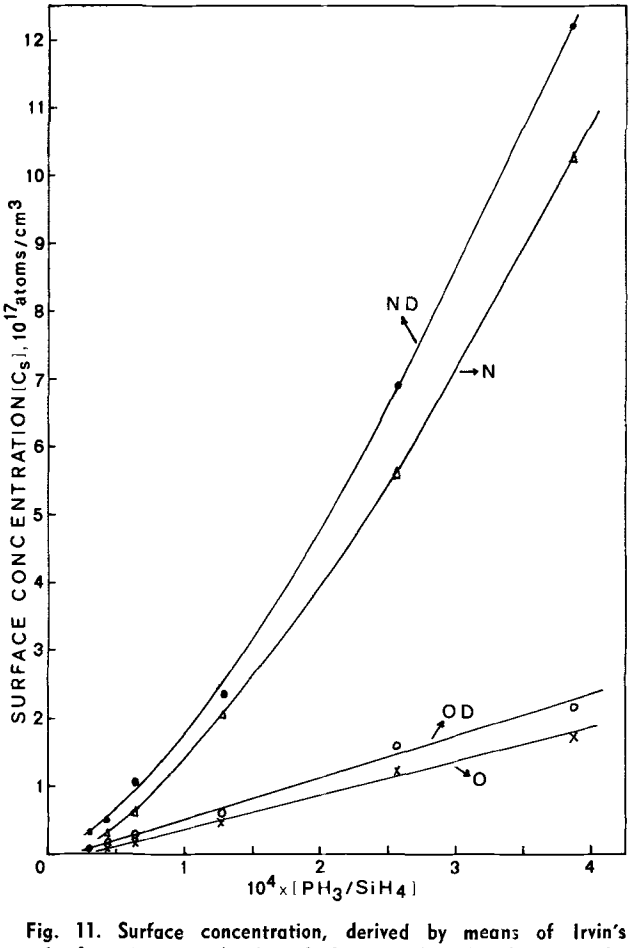

Fig. 11. Surface concentration, derived by means of Irvin's graphs from junction depth and sheet conductivity data, *vs.* the PH_3/SiH_4 ratio in the deposition gas. See Fig. 9 and 10.

and those in O_2 of about 1700Å. If we assume that the ratio P/Si in the oxide is the same as in the deposition gas, then $C_0/C_s = \sqrt{D_2/D_1}$ at 1200°C can be calculated. A value between 11 and 13 is found. Then in the case of N_2, x_B would be 67Å. This value is fairly large, as we expected (2, 5) a value of about 30Å. It may therefore be concluded that at 325°C relatively more P is deposited than according to the ratio PH_3/SiH_4.

We expected to find a larger value of the effective x_B in the case of an O_2 ambient during the drive-in but the theory is lacking for further analysis.

The difference between $(R_s)^{-1}$ in N_2 with or without a barrier corresponds, according to the theory, with $q\mu C_s x_B \sqrt{D_2/D_1}$. From this result we also derived a value for $x_B\sqrt{D_2/D_1}$. It was 900Å. This value agrees with the 800Å derived from the junction depth measurements. These values show that the theory gives a consistent description of the diffusion process. An application of these diffusion sources with low dopant concentration is shown in Fig. 12. To prevent (13) parasitic channels in p-channel MOS integrated circuits the active regions are surrounded by an area where the surface concentration of the substrate is increased by a diffusion from a phosphorus-doped layer.

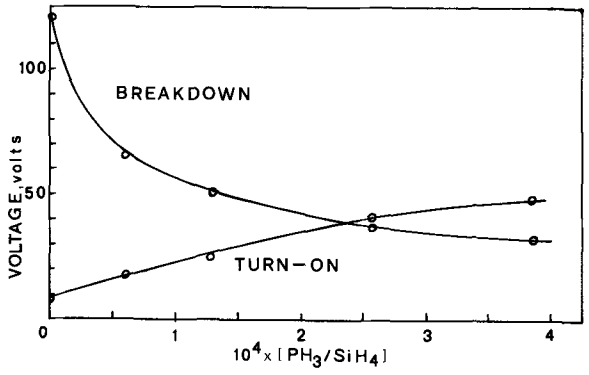

Fig. 12. Breakdown voltage of the drain of a MOS transistor and the parasitic turn-on voltage vs. the PH_3/SiH_4 ratio in the deposition gas for the doped oxide from which a diffusion takes place during the thermal growth of the gate oxide at 1200°C. Field oxide thickness: 8000Å.

The result is that the parasitic turn-on voltage increases. An adverse effect is that the breakdown voltage of the diffused areas decreases. A compromise is found when according to Fig. 12, the turn-on voltage and the breakdown voltage are both 40V. It is interesting to note that measurements of the turn-on voltage or C-V plots give an independent method of determining the surface concentrations. The values may be compared with those obtained by means of Irvin's graphs (8). In our experience the agreement is satisfactory but we do not consider these methods more accurate than Irvin's evaluation.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1974 JOURNAL.

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The Synthesis and Photoluminescence of $M^{II}M_2^{III}(S,Se)_4$

P. C. Donohue and J. E. Hanlon[1]

Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

ABSTRACT

The compositions $M^{II}M_2^{III}(S,Se)_4$ where M^{II} = Eu, Yb, Ca, Sr, Ba and M^{III} = Al, Ga, In were prepared by reaction of the elements in evacuated silica tubes with iodine as a mineralizer. All members except $Ba(Ga,Al)_2S_4$, which is cubic, exhibit the pseudo-orthorhombic $PbGa_2Se_4$ type structure. They are high resistivity p-type semiconductors; they exhibit Eu^{+2}-activated fluorescence which varies from red to blue as the electropositive character of the cations increase. Fluorescence activated by Yb^{+2} is seen at low temperature. Studies were made of the fluorescence decay lifetimes, temperature dependence, excitation spectra, and optical adsorption of $SrGa_2S_4$:Eu in order to relate the Eu^{+2}-activated fluorescence to the host bandgap. It is concluded that the most efficient phosphors are those in which the Eu^{+2} excited states lie farthest from the fundamental edge.

Sulfides and selenides of general formula $M^{II}M_2^{III}(S,Se)_4$ where M^{II} and M^{III} are divalent and trivalent cations, respectively, form a variety of structures (1,2). The most common are the Ag_2HgI_4 type, spinel type, Th_3P_4 type, and $CaFe_2O_4$ type. The spinel type is favored by smaller cations while the Th_3P_4 and $CaFe_2O_4$

[1] Deceased.

Key words: Eu^{+2} and Yb^{+2} activated photoluminescence of $M^{II}(Al,Ga,In)_2(S,Se)_4$.